

ELECTROCHEMICAL SENSOR FOR SCALE BUILDING UP MEASUREMENTS

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2

3 The present invention relates to an electrochemical
4 sensor apparatus and method and, in particular to an
5 electrochemical sensor that can be used to measure scale,
6 such as mineral scale or other particulates, which
7 deposit on the surface of pipelines or process equipment.

8

9 Mineral scale formation is one of the major flow
10 assurance concerns in the chemical industry. The problem
11 of scale build up arises where a fluid is flowing through
12 a pipe or vessel and particulates precipitate out from
13 the fluid and deposit on the surfaces of fluid-carrying
14 equipment. This can cause a blockage to form and to the
15 eventual failure of the equipment or disruption in the
16 flow of the fluid.

17

18 This problem is particularly apparent in the offshore oil
19 and gas industry. If the formation of scale or other
20 particulate masses goes uncontrolled, the operational
21 safety of the process or plant equipment can be
22 compromised through the failure of subsea safety and flow
23 control valves or other process equipment. If, for

1 example, a large mass of mineral scale forms in the riser
2 from an oil well, the mass of scale will cause the riser
3 to be blocked, consequently the flow of oil well fluids
4 will be impeded and the pressure will greatly increase,
5 thereby causing the riser to break.

6
7 In view of this problem, it is desirable to be able to
8 measure the amount of scale that has formed within a
9 conduit or vessel, and also to be able to estimate and
10 monitor the changes of likelihood that a fluid will
11 precipitate out scale or other particulates. A
12 measurement of the surface deposition on control surfaces
13 or changes of scaling tendency will alert the operator to
14 a build-up of scale. Hence, the operator of the well or
15 chemical process will be able to treat the fluid in order
16 to prevent scaling.

17
18 Current methods for monitoring the extent of surface
19 scaling and the scaling tendency in reservoirs or pipes
20 have limitations. They tend to involve measuring water
21 or other fluid samples, or to involve the measurement of
22 flow variables such as pressure. These methods do not
23 allow the operator to predict whether scaling will occur.
24 Scale detection often comes too late using this type of
25 monitoring, typically after a decrease in production. In
26 general, efforts to control the scaling problem have
27 concentrated upon strategies to mechanically or
28 chemically remove scale.

29
30 It is an object of the present invention to develop an
31 electrochemical sensor that allows the operator to
32 measure the extent of scale formation on a surface and to
33 assess the scaling tendency of a fluid.

1

2 In accordance with a first aspect of the present
3 invention, there is provided an electrochemical sensor
4 comprising:
5 an electrochemical cell having a sensor means;
6 fluid flow control means positioned so as to release a
7 fluid jet onto the sensor means, the fluid flow control
8 means having means for controlling the velocity of the
9 fluid jet, the fluid flow velocity being defined by the
10 Reynolds number of the fluid when the fluid is in the
11 fluid flow control means; and
12 wherein control of the Reynolds number and measurement of
13 the electrical output of the sensor provide a measure of
14 the build-up of scale on the working electrode.

15

16 Preferably, the measure of scale build up quantifies the
17 scale build up on the sensor surface in the
18 electrochemical cell.

19

20 Preferably, the sensor detects scale build up to measure
21 the scaling tendency of the fluid.

22

23 Preferably, the fluid control means is a conduit provided
24 with a control valve or pump.

25

26 Preferably, the sensor measures the change in electrical
27 output as a function of Reynolds Number during use of the
28 fluid flow control means

29

30 Preferably, the electrical output measurement means
31 measures the limiting current response of the sensor as a
32 function of Reynolds Number.

33

1 Preferably, the fluid flow control means is a conduit
2 having a predefined diameter (d) and is positioned at a
3 height (H) above the sensor having a radius (r).
4

5 Preferably, laminar flow of the fluid from the fluid
6 control means is provided by setting said diameter (d),
7 height (H) and radius (r).
8

9 Preferably, $H/d = 1$; and $r/d < 0.5$.
10

11 Preferably, the apparatus of the present invention
12 further comprises fluid sampling means for obtaining a
13 sample of a test fluid.
14

15 Preferably, the fluid sampling means contains fluid
16 isolation means for isolating the test fluid from a bulk
17 fluid.
18

19 Preferably, the test fluid isolation means is provided by
20 a container having at least one sealable valve which,
21 when opened, allows the test fluid to enter the sampling
22 means.
23

24 Preferably, the fluid flow control means comprises a flow
25 meter or flow sensor for measuring flow, connected to a
26 conduit from which said fluid jet is expelled.
27

28 Preferably, the sensor comprises a working electrode, a
29 counting electrode and a reference electrode.
30

31 Preferably, the electrochemical sensor further comprises
32 a reservoir for storing a second, pre-prepared
33 electrolyte, flow control means and one or more conduits

1 connected to the electrical cell such that the pre-
2 prepared electrolyte is used with the electrical cell to
3 measure the quantity of scale deposited by the test fluid
4 by measuring the electrical output of the cell as a
5 function of Reynolds Number.

6
7 In some examples of the present invention it has been
8 found that quantitative measurement of the extent of
9 scaling is more accurately determined by replacing the
10 test fluid with said pre prepared electrolyte in order to
11 make measurements.

12
13 Preferably, the electrolyte is a solution.

14
15 Preferably, the electrolyte is a solution of brine
16 containing a suitable tracer.

17
18 Preferably, the tracer is oxygen.

19
20 Optionally, the tracer is an ion tracer.

21
22 Optionally, the tracer is $Fe(CN)_6^{4-}$.

23
24 Preferably, the pre-prepared solution has a saturation
25 ratio of less than 1.

26
27 Optionally, the pre-prepared solution has a saturation
28 ratio of greater than 1.

29
30 In accordance with a second aspect of the present
31 invention, there is provided a method of measuring the
32 scaling properties of a test fluid, the method comprising
33 the steps of:

1 controlling the velocity of a fluid jet as defined by the
2 Reynolds number of the fluid when the fluid is in a fluid
3 flow control means;
4 releasing the fluid jet from the fluid control means onto
5 a sensor of an electrochemical cell; and
6 measuring the electrical output from the sensor as a
7 function of the Reynolds number of the jet fluid, the
8 sensor being in contact with a sample of the test fluid.
9

10 Preferably, the sensor gives a measure of the change in
11 electrical output as a function of Reynolds number during
12 use of the fluid flow control means.
13

14 Preferably, the electrical output provides a measure of
15 the limiting current response of the electrochemical cell
16 as a function of Reynolds Number.
17

18 Preferably, the fluid flow control means is a conduit
19 having a predefined diameter (d) and is positioned at a
20 height (H) above the working electrode or sensor having a
21 radius (r).
22

23 Preferably, laminar flow of the fluid from the fluid
24 control means is provided by setting said diameter (d),
25 height (H) and radius (r).
26

27 Preferably, $H/d = 1$; and $r/d < 0.5$.
28

29 Preferably, the test fluid has a saturation ratio of
30 greater than 1.

31 Preferably, the pre-prepared electrolyte is a conductive
32 Brine solution containing an oxygen tracer.
33

1 Optionally, the method comprises the further step of
2 isolating the test fluid from a flowing fluid prior to
3 measuring the electrical output from the electrical cell
4 as a function of the Reynolds number of the fluid.

5

6 Preferably, the test fluid is isolated by closing valves
7 arranged upstream and downstream of a predetermined
8 measuring location in a sample measuring means.

9

10 It has been found that isolation of a sample of the fluid
11 allows the fluid velocity as defined by the Reynolds
12 Number to be carefully controlled in the sensor device.

13

14 Preferably the fluid is isolated by removably attaching a
15 sampling conduit to a first conduit in which the bulk of
16 the fluid is situated, and by providing valves to isolate
17 the sampling conduit from the first conduit.

18

19 In accordance with a third aspect of the present
20 invention there is provided a method of measuring the
21 scaling properties of a test fluid, the method comprising
22 the steps of:

23 introducing a jet of test fluid into an electrochemical
24 cell so as to allow scale to build up on one or more
25 surfaces in the cell;

26 removing the test fluid from the electrochemical cell;

27 introducing a pre-prepared solution into the cell; and

28 measuring the electrical output from the electrochemical
29 cell.

30

31 Preferably, the test fluid is introduced into the
32 electrochemical cell at a rate defined by the Reynolds

1 Number of the fluid when contained in a first fluid
2 control means.

3

4 Preferably, the pre-prepared solution is introduced into
5 the electrochemical cell at a rate defined by the
6 Reynolds Number of the fluid when contained in a second
7 fluid control means.

8

9 Preferably, the electrical output measures the change in
10 electrical output as a function of Reynolds Number during
11 use of the fluid flow control means.

12

13 Preferably, the electrical output provides a measure of
14 the limiting current response of the electrochemical cell
15 as a function of Reynolds Number.

16

17 Preferably, the fluid flow control means is a conduit
18 having a predefined diameter (d) and is positioned at a
19 height (H) above the working electrode or sensor having a
20 radius (r).

21

22 Preferably, laminar flow of the fluid from the fluid
23 control means is provided by setting said diameter (d),
24 height (H) and radius (r).

25

26 Preferably, $H/d = 1$; and $r/d < 0.5$.

27

28 Preferably, the pre-prepared solution has a saturation
29 ratio of less than 1.

30

31 Optionally, the pre-prepared solution has a saturation
32 ratio of greater than 1.

33

1 In accordance with a fourth aspect of the present
2 invention, there is provided a computer program for use
3 with apparatus of the first aspect of the present
4 invention, and with the method of the second aspect of
5 the present invention, in which analysis of the
6 electrical output and the Reynolds number provides
7 information on the quantity of scale build up and/or the
8 scaling tendency of the fluid.

9

10 The present invention will now be described by way of
11 example only, with reference to the accompanying
12 drawings, in which:

13

14 Figure 1 is a schematic diagram of an embodiment of the
15 apparatus of the present invention;

16

17 Figure 2 is a graph of the limiting current output of the
18 electrochemical cell, as measured against the square root
19 of the Reynolds Number of the jet fluid;

20

21 Figure 3a is a graph of limiting current v Reynolds
22 number which shows it's variation after scaling has
23 occurred, figures 3b and 3c illustrate physical changes
24 to the sensor before and after scaling;

25

26 Figure 4 shows the relationship between the nozzle 12
27 from which the impinging jet emanates and the sensor 22

28

29 Figure 5 is a schematic representation of the second
30 embodiment of the present invention, where the
31 electrochemical cell is positioned in a conduit,
32 removably connected to a riser;

33

1 Figure 6 shows the limiting current correlation with
2 scaling index of the water;

3

4 Figure 7 is a schematic diagram of a third embodiment of
5 the present invention;

6

7 Figure 8 is a graph showing the current response to pre-
8 prepared brine solutions having different saturation
9 ratios; and

10

11 Figure 9 is a graph showing the correlation between the
12 saturation ratio for sample solutions and the slope of
13 the current similar to that of figure 8.

14

15 Figure 1 shows an electrochemical sensor setup comprising
16 an electrochemical cell rig 3, having the following
17 components. The electrochemical cell rig 3 comprises a
18 sensor (working electrode) 21 position proximate and
19 normal to the nozzle 9 through which a fluid jet (also
20 known as an impinging jet) exits from the nozzle 9. In
21 addition, the cell rig 18 provides support for a
22 reference electrode (silver-silver electrode) 19 and a
23 counting electrode 23 made of platinum, in this example.

24

25 The fluid control means consists of a pump 15 positioned
26 downstream of a needle valve 13 which is used to control
27 the flow level of the impinging jet fluid. A flow meter
28 7 is used to measure the amount of flow of the impinging
29 jet fluid so as to allow calculation of the Reynolds
30 number of the jet fluid. A nozzle 9 provides the means
31 by which the impinging jet fluid exits the fluid control
32 means 5 and contacts the working electrode 21. In this

1 example, a solution tank is provided for storage and
2 circulation of the impinging jet fluid.

3

4 Figure 2 is a graph of the limiting current i_L measured
5 against the square root of Reynolds Number ($Re^{1/2}$). The
6 graph 41 shows three curves. The first curve illustrates
7 a situation in which no scale has been deposited upon the
8 working electrode from the test fluid. Curve 45
9 illustrates the situation on an unscaled sensor. Curves
10 46, 47 and 48 illustrate the response from the sensor
11 with 22%, 39% and 46% of scale coverage respectively
12 after immersion for 1, 9 and 24 hours in a scaling
13 solution. These schematic representations show the
14 difference in the limiting current over the same range of
15 Reynolds number, where the level of scaling in the sample
16 is different.

17

Immersion Time,Hrs	%Scale Coverage
1	22
9	39
24	46

18

19 Table 1 shows the resultant scale coverage for different
20 immersion times.

21

22 In use, the fluid control means or impinging jet system 5
23 is submerged in a fluid sample, and is used to control
24 the hydrodynamic regime at the surface of the working
25 electrode 21. Through analysis of the oxygen tracer
26 reduction reaction on the sensor surface, the extent of
27 scaling and the scaling tendency of the fluid can be
28 determined. In this example the test solution has a
29 saturation ratio of greater than 1 and is used to deposit

1 scale on the sensor surface. A pre-prepared electrolyte
2 is used to determine the scale coverage.

3

4 The potential of the electrochemical sensor 1 is applied
5 to -0.8 volts (with respect to a silver/silver chloride
6 system) when measurements are started. The impinging jet
7 system is then controlled through a range of Reynolds
8 numbers, and the limiting current response is measured as
9 a function of the Reynolds number. Measuring the
10 relationship between these two variables, enables scaling
11 information to be obtained. In this way, the amount of
12 scale and the scaling tendency of the test fluid can be
13 determined.

14

15 Figure 6 shows the limiting current correlation with
16 scaling index (log of saturation ratio) of the test fluid
17 (water containing electrolyte) for 6000s. The
18 correlation between the scaling index and the
19 electrochemical measurement make it possible to measure
20 the scaling tendency of a fluid.

21

22 Figures 3 a to c and 4 provide more detailed explanation
23 of a sensor in accordance with the present invention.

24

25 Figure 3a is a graph 2 of limiting current versus
26 Reynolds Number^{1/2} on a sensor. Two curves 4 and 6
27 illustrate the change in limiting current as a function
28 of Reynolds number from initial values (curve 4) to final
29 values (curve 6).

30

31 Figure 3b shows the sensor surface 8 before the use of
32 the impinging jet which emanates from the nozzle, and
33 figure 3c shows the sensor surface after this operation.

1 The surface can be seen to be patchy as a result of scale
2 coverage.

3

4 Limiting current is given as follows:

5
$$I_{lim} = K Re^{1/2}$$

6

7 The a measure of the scale coverage on the sensor is
8 given by:

9
$$\text{Scale coverage} = (K_i - K_f) / K_i$$

10

11 Figure 4 shows the relationship between the nozzle 12
12 from which the impinging jet emanates and the sensor 22.
13 The nozzle has an inner diameter d 14 and the nozzle is
14 placed at a distance H 16 from the sensor 22. Laminar
15 flow of the surface impinging jet occurs where:

16

17 $H/d = 1$; and

18 $r/d < 0.5$.

19

20 Figure 5 shows a second embodiment of the present
21 invention, in which the cell rig is installed in the
22 bypass system of a sub-sea pipeline. The arrows 32 show
23 the direction of fluid flow through the system. The fluid
24 flow rate as quantified by calculation of the Reynolds
25 number is controlled through valves 37, 39 located in the
26 inlet and outlet of the bypass.

27

28 As shown in Figure 5, the bulk fluid 33 flows down
29 conduit 31 and a sample (the test fluid) of the bulk
30 fluid 33 is tapped from the bulk fluid conduit 31 to
31 measurement conduit or bypass system 35. Once the test
32 fluid has been tapped, valves 37 and 39 are used to
33 control the fluid flow rate into the cell 3 where scale

1 is deposited on the working electrode 21. The working
2 electrode (sensor) 21 is connected to a potentiostat (not
3 shown)A flow meter (not shown) measures the flow rate. In
4 this example, to enable measurements of the extent of
5 scale to be made, the impinging jet is directed onto the
6 working electrode 21 and the fluid surrounding the sensor
7 is essentially static.

8

9 The output current from the electrochemical cell 3 over a
10 period of time enables the scaling tendency to be
11 measured. Accordingly, the likelihood and speed with
12 which scale is likely to precipitate out from the bulk
13 fluid can be estimated.

14

15 The ability to operate the electrochemical sensor of the
16 present invention in situ allows the scaling tendency to
17 be monitored as the pressure, temperature, water
18 chemistry and other environmental conditions change. By
19 locating the apparatus of the present invention within
20 the precise zone of interest within a pipeline, the
21 present invention can monitor the scaling tendency from
22 individual branches of a pipe in, for example, a
23 horizontal well which goes into the main pipeline.
24 Information feedback from the well can provide an early
25 indication of scaling potential problems. Hence, the
26 present invention enables the operator to manage and
27 selectively control individual wells and to inject the
28 correct amount of scale inhibitor in these wells.

29

30 Further advantageously, the present invention can detect
31 small amounts of scale and can rapidly (within a matter
32 of 30 minutes or so) determine the scaling tendency of
33 the sample. As a consequence, the operator of the

1 conduit, whether it be a riser from an oil well, a subsea
2 pipeline, a pipe in a desalination plant, or otherwise,
3 can quickly determine the scaling tendency in these
4 positions and can anticipate problems associated with the
5 build up of scale.

6
7 In use, the apparatus of the present invention will be
8 connected to an operator terminal by means of a suitable
9 telemetry system. This will allow data to be collected
10 frequently by the operator using a communications
11 protocol. Real-time data from the oil well or other
12 location will be sent to a PC based surface system that
13 monitors this location. In addition, multiple systems
14 can be used at varying locations in a pipeline system or
15 well or the like, and all of these individual systems can
16 feed data back to a single PC for analysis by the
17 operator, who may then use this data to determine it is
18 necessary to add chemical scale inhibitors to that
19 location, or to otherwise remove or limit the scale
20 measured at that location.

21
22 Figure 7 shows a further embodiment of the present
23 invention similar to that shown in Figure 7. Figure 7 is
24 an embodiment of the invention in which a pre-prepared
25 solution is used when measuring the scale coverage of a
26 working electrode. The sensor arrangement 51 has two
27 fluid flow paths 53 and 55.

28
29 Flow path 53 is similar to the flow path shown in figure
30 7 and allows a fluid sample to be taken from a pipe 57
31 and fed through an electrochemical cell 61 via a conduit
32 59. Flow path 55 includes a solution tank 63 and a pump
33 69 which allow the supply of a pre-prepared electrolyte

1 (brine in this example) to the electrochemical cell rig.
2 It has been found that the use of this electrolyte allows
3 a more accurate measure of the scale coverage to be
4 achieved as the electrolyte is pre-prepared and
5 substantially free from the contaminants that are often
6 found in the bulk fluid contained in the pipeline 57.

7
8 A potentiostat 65 is used to measure the electrical
9 output of the electrochemical cell and this is connected
10 to a personal computer or network 69 by means of a
11 suitable connection. This allows the end user to monitor
12 the scale coverage or scaling tendency from an office or
13 lab.

14
15 In order to measure scale coverage using this example of
16 the present invention, test fluid from the pipeline 57 is
17 fed into the electrochemical cell 61 via the conduit 59
18 and the control valve 58 such that the test fluid
19 continuously impinges upon the sensor surface 62. Valves
20 58 and 60 are used to control the rate at which the which
21 test fluid enters the cell, the flow is measured by a
22 flow meter (not shown) from which the Reynolds number can
23 be calculated. At this stage, the electrical output of
24 the cell 61 is not measured however, as the rate of test
25 fluid entry into the cell is a variable in the system, it
26 is desirable to control and measure this variable as it
27 shows the extent to which the flow is laminar or
28 turbulent. The test fluid flow is controlled so that it
29 continuously impinges upon the sensor surface 62 (working
30 electrode) for a predetermined period of time and scale
31 is deposited onto the sensor surface 62.

32

1 The extent of scale on the surface 62 is measured using
2 the pre-prepared electrolyte (typically an electrolytic
3 solution such as brine) and is provided to the cell 61
4 via flow path 55. The brine solution is pumped
5 continuously through the cell 61 in a controlled manner
6 such that the Reynolds Number of the flowing brine can be
7 measured. The scale coverage of the sensor 62 is
8 measured using the potentiostat 65 to record the output
9 current of the cell 61.

10

11 In this example of the present invention, the scaling
12 tendency of the test fluid is measured as follows. Test
13 fluid from the pipeline 57 is fed into the
14 electrochemical cell 61 via the conduit 59 and the
15 control valve 58 such that the test fluid continuously
16 impinges upon the sensor surface 62. Valves 58 and 60 are
17 used to control the rate at which the test fluid enters
18 the cell. The Reynolds Number can therefore be
19 calculated.

20

21 The current output of the cell 61 is measured as a
22 function of time and the scaling tendency can be
23 calculated and provided to a user through the PC or
24 network 69.

25

26 Figure 8 is a graph 73 showing the current response
27 (current density) as a function of time for electrolytic
28 solutions (brine) having different saturation ratios.
29 The saturation ratios for curves 75, 77, 79 and 81 are
30 17.8, 8.91, 0.27 and 1.09 respectively. Curve 79 has a
31 negative gradient.

32

1 Figure 9 is a graph 83 which illustrates the correlation
2 between saturation ratio and the slope of the current
3 values against time as exemplified in figure 8.
4 Curve 85 shows that scaling of the fluid does not occur
5 in region 89 where the saturation ratio is below
6 approximately 1 and scaling does occur in region 87 of
7 the graph 83 where the scaling ratio is above
8 approximately 1. This region is where the fluid is
9 supersaturated.

10

11 The present invention has a number of advantages over the
12 known prior art. In particular, the present invention
13 allows early measurement of scale or other particulates,
14 and provides a means by which the scaling tendency of the
15 fluid in question can be measured. Measurement of the
16 scaling tendency, as well as the bulk amount of scale,
17 allows the operator to predict the amount of inhibitor
18 that should be used, and also to predict when in the
19 future this inhibitor should be applied.

20 Improvements and modifications may be incorporated
21 herein, without deviating from the scope of the
22 invention.